

**DIFFRACTION INVESTIGATIONS OF CEMENT CLINKER AND
TRICALCIUM SILICATE USING RIETVELD ANALYSIS**

Vanessa Kate Peterson

Bachelor of Applied Science (Honours) in Chemistry with First Class Honours

Department of Chemistry, Materials and Forensic Sciences

University of Technology, Sydney

August 2003

Submitted for the Degree of Doctor of Philosophy

CERTIFICATE OF AUTHORSHIP / ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidate

Vanessa Peterson

ACKNOWLEDGMENTS

I am grateful to Dr Brett Hunter from the Australian Nuclear Science and Technology Organisation (ANSTO) for help and guidance during his role as supervisor. Thanks to Bragg Institute staff of ANSTO, for various discussions, and to A/Prof. Abhi Ray from the University of Technology, Sydney (UTS). I also thank Dr Ray Withers from the Australian National University for help with work involving structural modulation.

This work was supported by an Australian Ph.D. award and a postgraduate research award from the Australian Institute of Nuclear Science and Engineering (AINSE). Thanks to the UTS for use of thermal analysis facilities. Use of neutron facilities at the ANSTO was funded by the AINSE. Thanks to the ANSTO for the use of other equipment. Facility use at the Australian National Beamline Facility, Japan, was funded by the Australian Synchrotron Research Program. Facility use at Brookhaven National Laboratories, U.S.A., was funded by the Access to Major Research Facilities program of the ANSTO.

I would like to thank those listed below, responsible for support to attend schools, conferences, meetings, and congresses. I was able to attend many during my doctoral candidature, and it is through these events that opportunities for the student to enter the research world as a working scientist begin.

- ANSTO.
- UTS.
- School on symmetry of crystals organising committee.
- International Union of Crystallography.
- Australian X-ray Analytical Association.
- Professor Brian O'Connor.
- Australian Institute of Physics.
- National Institute of Standards and Technology
- Society of Crystallographers in Australia and New Zealand.
- Australian synchrotron project.

Thanks to my mum and to all of my friends, especially Dr Mikl Law. Final thanks goes to the world of rock climbing, which kept me inspired as a scientist.

TABLE OF CONTENTS

CERTIFICATE OF AUTHORSHIP/ORIGINALITY	i
ACKNOWLEDGMENTS	ii
LIST OF FULLY REVIEWED PUBLICATIONS	vii
LIST OF FIGURES	viii
LIST OF TABLES	xii
LIST OF ABBREVIATIONS.....	xv
 ABSTRACT	 xvii
 CHAPTER 1: RESEARCH OBJECTIVES AND THESIS OVERVIEW	
1.1 Introduction	1
1.2 Research issues and investigations	2
1.3 Structure of the thesis.....	3
 CHAPTER 2: CEMENT STRUCTURE AND CHEMISTRY	
2.1 Introduction	5
2.2 Crystal chemistry of Portland cement	5
2.3 Crystal modification of clinker components	6
2.3.1 Tricalcium silicate modifications.....	7
2.3.2 Dicalcium silicate modifications.....	23
2.3.3 Tricalcium aluminate modifications	27
2.3.4 Tetracalcium aluminoferrite modifications.....	29
2.3.5 Phases of Portland cement	30
2.4 Phase quantification of cement clinker	32
2.4.1 Amorphous clinker components	34
2.5 Hydration of Portland cement	35
2.5.1 Hydration of calcium silicates.....	36
2.5.2 Strength of hydrated tricalcium silicate	39
2.5.3 Hydration of tricalcium aluminate	40
2.5.4 States of water in cement paste	42

CHAPTER 3: THEORETICAL BACKGROUND AND EXPERIMENTAL METHODS

3.1	Introduction	44
3.2	Crystal structure	45
3.3	Diffraction	46
3.3.1	Miller indices and Bragg theory	47
3.3.2	Neutron and X-ray scattering	49
3.3.3	Modulated crystal structures	54
3.4	Powder diffraction	56
3.5	Radiation sources	59
3.5.1	Laboratory X-ray sources	59
3.5.2	Synchrotron sources	60
3.5.3	Neutron sources	62
3.6	Rietveld analysis	65
3.6.1	Core mathematics in Rietveld refinement	66
3.6.2	Combined X-ray and neutron Rietveld refinement	72
3.6.3	Rietveld refinement programs Rietica, GSAS, and JANA	73
3.6.4	Pattern decomposition analysis	75
3.7	Electron diffraction	76
3.8	X-ray fluorescence	77
3.9	Differential thermal analysis	79

CHAPTER 4: QUANTITATIVE PHASE DETERMINATION OF CEMENT CLINKER USING THE RIETVELD METHOD

4.1	Introduction	82
4.2	Comparison of diffraction sources	83
	Peterson <i>et al</i> (2002a)	85
	Peterson <i>et al</i> (2002b)	89
4.3	Summary	111

CHAPTER 5: COMPLICATIONS OF CEMENT CLINKER ANALYSIS USING THE RIETVELD METHOD

5.1	Introduction	113
5.2	Modelling of minor phases into the Rietveld analysis of cement	114

	Peterson <i>et al</i> (2003a)	115
5.3	Structural deviations of tricalcium silicate in clinker	121
	Peterson <i>et al</i> (2002c)	122
5.4	Summary	126
CHAPTER 6: STRUCTURAL INVESTIGATION OF TRICALCIUM SILICATE		
6.1	Introduction	128
6.2	Polymorphic investigations	130
6.2.1	Neutron investigation of polymorphism	130
6.2.2	Synchrotron investigation of polymorphism at the High Energy Accelerator Research Organisation, Japan.....	134
6.2.3	Synchrotron investigation of polymorphism at the National Synchrotron Light Source, USA	137
	Peterson <i>et al</i> (2003b)	138
6.3	Structural modulation in tricalcium silicate	164
6.3.1	Formulation of the parent sub-structure	165
6.4	Summary	171
CONCLUSIONS AND FUTURE RESEARCH.....		173
APPENDIX A: CRYSTAL STRUCTURES OF CLINKER COMPONENTS.....		174
A1	Crystal structures for tricalcium silicate	174
A1.1	T ₁ C ₃ S structure Ca ₃ (SiO ₄)O determined by Golovastikov <i>et al</i> (1975)	174
A1.2	M ₃ C ₃ S structure Ca _{2.89} Mg _{0.11} (SiO ₄)O determined by Nishi <i>et al</i> (1985)	177
A1.3	M ₃ C ₃ S structure Ca _{2.99} Na _{0.01} (Si _{0.90} Al _{0.04} Fe _{0.02} P _{0.03} Mg _{0.05})O ₅ determined by Mumme (1995)	183
A1.4	R C ₃ S structure Ca ₃ (SiO ₄)O determined by Il'inets <i>et al</i> (1985)	184
A1.5	R C ₃ S structure Ca _{2.98} Si _{0.98} Al _{0.04} O ₅ determined by Nishi <i>et al</i> (1985)	185
A1.6	R C ₃ S structure Ca ₃ (SiO ₄)O determined by Jeffery (1952)	186
A2	Crystal structures for dicalcium silicate	187
A2.1	β C ₂ S structure Ca ₂ SiO ₄ determined by Mumme <i>et al</i> (1995).....	187

A3	Crystal structures for tricalcium aluminate	188
A3.1	Cubic C ₃ A Ca ₉ (Al ₆ O ₁₈) structure determined by Mondal and Jeffery (1975)	188
A3.2	Cubic C ₃ A Ca _{8.688} Na _{0.625} (Al ₆ O ₁₈) structure determined by Takéuchi <i>et al</i> (1980).....	189
A3.3	Orthorhombic C ₃ A Ca _{8.5} NaAl ₆ O ₁₈ structure determined by Nishi and Takéuchi (1975)	190
A3.4	Orthorhombic C ₃ A Ca _{8.393} Na _{0.875} (Al _{5.175} Fe _{0.45} Si _{0.375} O ₁₈) structure determined by Takéuchi (1980).....	191
A3.5	Monoclinic C ₃ A structure Ca _{8.25} Na _{1.5} (Al ₆ O ₁₈) determined by Takéuchi <i>et al</i> (1980).....	192
A4	Crystal structures for tetracalcium aluminoferrite	194
A4.1	Orthorhombic C ₄ AF structure Ca ₂ (Fe _{1.28} Al _{6.72})O ₅ determined by Colville and Geller (1972).....	194
APPENDIX B: MATERIALS AND EXPERIMENTAL		
B1	Characterisation of tricalcium silicate from Construction Technology Laboratories (CTL)	195
B1.1	XRF analysis of tricalcium silicate from CTL.....	195
B1.2	Rietveld analysis of tricalcium silicate from CTL	197
B1.3	DTA analysis of tricalcium silicate from CTL	209
B2	Characterisation of tricalcium silicate synthesised at ANSTO	211
B2.1	Method of tricalcium silicate synthesis.....	212
B2.2	XRF analysis of tricalcium silicate synthesised at ANSTO	212
B2.3	Rietveld analysis of tricalcium silicate synthesised at ANSTO.....	213
B2.4	DTA analysis of tricalcium silicate synthesised at ANSTO	221
B3	Calibration of furnace at BNL from Chapter 6, section 6.2.3.....	223
REFERENCES		224

LIST OF FULLY REFEREED PUBLICATIONS

1. Peterson *et al* (2002a) **published** page 85
V. Peterson, B. Hunter, A. Ray, and L.P. Aldridge
Rietveld refinement of neutron, synchrotron and combined powder diffraction data of cement clinker
Applied Physics A **74** [Suppl.], S1409 -S1411 (2002).
2. Peterson *et al* (2002b) **under review** page 89
V.K. Peterson, B. Hunter, and A. Ray
Quantitative phase analysis of cement clinker using Rietveld analysis: comparison of results from various sources
Journal of the American Ceramic Society, (2002).
3. Peterson *et al* (2002c) **published** page 122
V.K. Peterson, B. Hunter, and A. Ray
Neutron diffraction investigation of structural deviations in cement clinker
Proceedings of the Australian Institute of Physics 15th Biennial Congress (Sydney 2002), 1-3, AIP, Sydney (2002).
4. Peterson *et al* (2003a) **published** page 115
V.K. Peterson, A. Ray, and B. Hunter
Importance of minor phase inclusion in the Rietveld analysis of cement clinkers
Proceedings of the 11th International Congress on the Chemistry of Cement (Durban 2003), 146-150, Cement and Concrete Institute, Durban (2003).
5. Peterson *et al* (2003b) **accepted** page 138
V.K. Peterson, B. Hunter, and A. Ray
Tricalcium silicate T₁ and T₂ polymorphic investigations: Rietveld refinement at various temperatures using synchrotron powder diffraction
Journal of the American Ceramic Society, (2003).

LIST OF FIGURES

CHAPTER 2

Figure 2.1: Hexagonal basal plane of the cell in pure Ca_3SiO_5	10
Figure 2.2: Monoclinic deformation of basal plane of the hexagonal cell in pure	11
Figure 2.3: Triclinic deformation of basal plane of the hexagonal cell in pure Ca_3SiO_5	11
Figure 2.4: Pseudo-hexagonal and pseudo-orthohexagonal axes deformation of basal plane of the hexagonal cell in pure Ca_3SiO_5	11
Figure 2.5: Crystal axes arrangement of the first and second representations of the each C_3S modification.	12
Figure 2.6: First unit cell representation of structure in C_3S type R (Jeffery, 1952)	13
Figure 2.7: Second unit cell representation of structure in C_3S type R (Jeffery, 1952)	13
Figure 2.8: First unit cell representation of structure in C_3S type R (Nishi and Takéuchi, 1984)	14
Figure 2.9: Second unit cell representation of structure in C_3S type R (Nishi and Takéuchi, 1984)	14
Figure 2.10: First unit cell representation of structure in C_3S type R (Il'inets <i>et al</i> , 1985)	15
Figure 2.11: Second unit cell representation of structure in C_3S type R (Il'inets <i>et al</i> , 1985)	15
Figure 2.12: First unit cell representation of structure in monoclinic C_3S type M_3 (Nishi and Takéuchi, 1984)	16
Figure 2.13: Second unit cell representation of structure in monoclinic C_3S type M_3 (Nishi and Takéuchi, 1984)	17
Figure 2.14: Third unit cell representation showing common basal plane within C_3S type M_3 (Nishi and Takéuchi, 1985), with crystal axes arrangement shown.....	17
Figure 2.15: First unit cell representation of structure in monoclinic C_3S type M_3 (Mumme, 1995)	18
Figure 2.16: Second unit cell representation of structure in monoclinic C_3S type M_3 (Mumme, 1995)	18

Figure 2.17: Third unit cell representation showing common basal plane within monoclinic C_3S type M_3 (Mumme, 1995), with crystal axes arrangement shown.....	19
Figure 2.18: First unit cell representation of structure in triclinic C_3S type T_1 (Golovastikov <i>et al</i> , 1975).....	19
Figure 2.19: Second unit cell representation of structure in triclinic C_3S type T_1 (Golovastikov <i>et al</i> , 1975).....	20
Figure 2.20: Third unit cell representation showing common basal plane within C_3S type T_1 (Golovastikov <i>et al</i> , 1975), with crystal axes arrangement shown.....	20
Figure 2.21: Crystal structure of α C_2S (Taylor, 1997)	24
Figure 2.22: Crystal structure of α'_H C_2S (Taylor, 1997).....	25
Figure 2.23: Crystal structure of β C_2S (Taylor, 1997).....	25
Figure 2.24: Crystal structure of γ C_2S (Taylor, 1997)	26
Figure 2.25: Unit cell of C_3A showing the Al_6O_{18} ring structure of Mondal and Jeffery (1975) (Taylor, 1997).....	27
Figure 2.26: Colville and Geller, (1972) structure of brownmillerite (Jupe <i>et al</i> , 2001)	30
Figure 2.27: Calorimetric plot of the rate of heat evolution with time for the hydration of OPC.....	35
Figure 2.28: Calorimetric plot of the rate of heat evolution with time for the hydration of C_3S (Young, 1983).....	38

CHAPTER 3

Figure 3.1: Two-dimensional representation of the periodic property in a crystal.....	46
Figure 3.2: Representation of the crystallographic planes hkl	47
Figure 3.3: Reciprocal space diagram representing Bragg scattering.....	54
Figure 3.4: X7A resolution function using Si(111)/Ge(220) double crystal monochromator and analyser (X7A external website)	62
Figure 3.5: X-ray and neutron nuclear scattering amplitudes	63

CHAPTER 6

Figure 6.1: Refinement plot of neutron data of C_3S at ambient temperature.....	131
Figure 6.2: Refinement plot of neutron data of C_3S at approximately 570 °C	131
Figure 6.3: Refinement plot of neutron data of C_3S at approximately 670 °C	131
Figure 6.4: Refinement plot of neutron data of C_3S at approximately 950 °C	132
Figure 6.5: Refinement plot of neutron data of C_3S at approximately 980 °C	132
Figure 6.6: Refinement plot of neutron data of C_3S at approximately 1035 °C	132
Figure 6.7: Refinement plot of neutron data of C_3S at approximately 1120 °C	133
Figure 6.8: Laboratory X-ray data showing of reflections of C_3S at ambient temperature	134
Figure 6.9: Synchrotron data showing reflections of C_3S at ambient temperature.....	135
Figure 6.10: Experimental set-up showing in-situ furnace on beam line 20B at the KEK synchrotron, Japan.....	135
Figure 6.11: Synchrotron data of C_3S at various temperatures taken on beam line 20B, KEK, Japan.....	136
Figure 6.12: Experimental set-up on beam line X7A at the NSLS, BNL, USA.....	137
Figure 6.13: First unit cell representation of structure in C_3S type R, trigonal in the rhombohedral setting (Jeffrey, 1952)	167
Figure 6.14: First unit cell representation of structure in C_3S type R, trigonal in the rhombohedral setting (Jeffrey, 1952)	167

APPENDIX B

Figure B1.1: Derivative-DTA data for the first heating and cooling cycle of triclinic C_3S from CTL.....	209
Figure B1.2: Derivative-DTA data for the second heating and cooling cycle of triclinic C_3S from CTL.....	210
Figure B1.3: Derivative-DTA data for the third heating and cooling cycle of triclinic C_3S from CTL.....	210
Figure B1.4: Derivative-DTA data for the fourth heating and cooling cycle of triclinic C_3S from CTL.....	211
Figure B2.1: First histogram refinement plot of Mg-stabilised triclinic C_3S using Rietica	214

Figure B2.2: Second histogram refinement plot of Mg-stabilised triclinic C ₃ S using Rietica	214
Figure B2.3: Unit cell representation with transformation showing common hexagonal plane of structure in Mg-stabilised C ₃ S, with crystal axes arrangement shown	215
Figure B2.4: Unit cell representation of structure in Mg-stabilised C ₃ S, with crystal axes arrangement shown	215
Figure B2.5: Derivative-DTA data for the first heating and cooling cycle of Mg-stabilised triclinic C ₃ S	221
Figure B2.6: Derivative-DTA data for the second heating and cooling cycle of Mg-stabilised triclinic C ₃ S.....	222
Figure B2.7: Derivative-DTA data for the third heating and cooling cycle of of Mg-stabilised triclinic C ₃ S.....	222
Figure B2.8: Derivative-DTA data for the fourth heating and cooling cycle of of Mg-stabilised triclinic C ₃ S	223
Figure B3.1: Calibration curve for furnace on beam-line X7A using NaCl.....	223

LIST OF TABLES

CHAPTER 2

Table 2.1:	Modifications of C_3S	7
Table 2.2:	Known structural modulations in C_3S (Urabe <i>et al</i> , 2000) (Urabe <i>et al</i> , 2002).....	22
Table 2.3:	Modifications of C_2S	23
Table 2.4:	Modifications of C_3A of the general formula $Na_{2x}Ca_{3-x}Al_2O_6$ (Takèuchi <i>et al</i> , 1980).....	28
Table 2.5:	Crystal data for the solid solution series $Ca_2(Al_xFe_{1-x})_2O_5$ (Taylor, 1997).....	29
Table 2.6:	Hydration sequence of calcium silicates (Taylor, 1997)	38
Table 2.7:	Formation of C_3A hydration products with varying amounts of $C\bar{S}H_2$ (Taylor, 1997)	42

CHAPTER 3

Table 3.1:	Summary of the High Resolution Powder Diffractometer (ANSTO website).....	64
------------	--	----

CHAPTER 6

Table 6.1:	Crystal constants for the rhombohedral sub-structure of C_3S	166
Table 6.2:	Atomic positions for the rhombohedral sub-structure of C_3S	166
Table 6.3:	Crystal constants for the unrefined sub-structure of C_3S T_1	168
Table 6.4:	Atomic positions for the unrefined sub-structure of C_3S T_1	169

APPENDIX A

Table A1.1:	Crystal constants for T_1 C_3S (Golovastikov <i>et al</i> , 1975).....	174
Table A1.2:	Atomic positional and displacement parameters for T_1 C_3S (Golovastikov <i>et al</i> , 1975).....	174
Table A1.3:	Crystal constants for M_3 C_3S (Nishi <i>et al</i> , 1985).....	177
Table A1.4:	Atomic positional and displacement parameters for M_3 C_3S (Nishi <i>et al</i> , 1985).....	177
Table A1.5:	Crystal constants for M_3 C_3S (Mumme, 1995).....	183
Table A1.6:	Atomic positional and displacement parameters for M_3 C_3S (Mumme, 1995).....	183

Table A1.7:	Crystal constants for R C ₃ S (Il'inets <i>et al</i> , 1985)	184
Table A1.8:	Atomic positional and displacement parameters for R C ₃ S (Il'inets <i>et al</i> , 1985)	184
Table A1.9:	Crystal constants for R C ₃ S (Nishi <i>et al</i> , 1985)	185
Table A1.10:	Atomic positional and displacement parameters for R C ₃ S (Nishi <i>et al</i> , 1985)	185
Table A1.11:	Crystal constants for R C ₃ S (Jeffery, 1952)	186
Table A1.12:	Atomic positional and displacement parameters for R C ₃ S (Jeffery, 1952)	186
Table A2.1:	Crystal constants for β C ₂ S (Mumme <i>et al</i> , 1995)	187
Table A2.2:	Atomic positional and displacement parameters for β C ₂ S (Mumme <i>et al</i> , 1995)	187
Table A3.1:	Crystal constants for cubic C ₃ A (Mondal and Jeffery, 1975)	188
Table A3.2:	Atomic positional and displacement parameters for cubic C ₃ A (Mondal and Jeffery, 1975)	188
Table A3.3:	Crystal constants for cubic C ₃ A (Takéuchi <i>et al</i> , 1980)	189
Table A3.4:	Atomic positional and displacement parameters for cubic C ₃ A (Takéuchi <i>et al</i> , 1975)	189
Table A3.5:	Crystal constants for orthorhombic C ₃ A (Nishi and Takéuchi, 1975) ..	190
Table A3.6:	Atomic positional and displacement parameters for orthorhombic C ₃ A (Nishi and Takéuchi, 1975)	190
Table A3.7:	Crystal constants for orthorhombic C ₃ A (Takéuchi <i>et al</i> , 1980)	191
Table A3.8:	Atomic positional and displacement parameters for orthorhombic C ₃ A (Takéuchi <i>et al</i> , 1975)	191
Table A3.9:	Crystal constants for monoclinic C ₃ A (Takéuchi <i>et al</i> , 1980)	192
Table A3.10:	Atomic positional and displacement parameters for monoclinic C ₃ A (Takéuchi <i>et al</i> , 1975)	192
Table A4.1:	Crystal constants for orthorhombic C ₄ AF (Colville and Geller, 1971)	194
Table A4.2:	Atomic positional and displacement parameters for orthorhombic C ₄ AF (Colville and Geller, 1971)	194

APPENDIX B

Table B1.1:	Composition of triclinic C_3S from CTL provided by CTL	195
Table B1.2:	XRF composition of triclinic C_3S from CTL by the bead method provided by the University of New South Wales.....	196
Table B1.3:	XRF composition of triclinic C_3S from CTL performed at ANSTO on a larger powder sample.....	196
Table B1.4:	XRF composition of triclinic C_3S from CTL performed at ANSTO on a smaller powder sample	197
Table B1.5:	Atomic positional and displacement parameters for the average sub-cell structure of T_1 triclinic C_3S T_1 from CTL at ambient temperature after refinement of synchrotron data from BNL	197
Table B1.6:	Si-O bond lengths of triclinic C_3S T_1 from CTL at ambient temperature after refinement of synchrotron data from BNL.....	199
Table B1.7:	O-Si-O bond angles of triclinic C_3S T_1 from CTL at ambient temperature after refinement of synchrotron data from BNL.....	200
Table B1.8:	Atomic positional and displacement parameters for the average sub-cell structure of T_1 triclinic C_3S T_1 from CTL at 549(21) ° C after refinement of synchrotron data from BNL	202
Table B1.9:	Si-O bond lengths of triclinic C_3S T_1 from CTL at 549(21) ° C after refinement of synchrotron data from BNL.....	204
Table B1.10:	O-Si-O bond angles of triclinic C_3S T_1 from CTL at 549(21) ° C after refinement of synchrotron data from BNL.....	205
Table B1.11:	Si-O bond lengths of triclinic C_3S T_1 from CTL at 682(28) ° C after refinement of synchrotron data from BNL.....	206
Table B1.12:	O-Si-O bond angles of triclinic C_3S T_1 from CTL at 682(28) ° C after refinement of synchrotron data from BNL	207
Table B2.1:	XRF composition of triclinic C_3S synthesised at ANSTO.....	213
Table B2.2:	Crystal constants for Mg-stabilised triclinic C_3S	216
Table B2.3:	Atomic positional and displacement parameters for Mg-stabilised triclinic C_3S	216
Table B2.4:	Si-O bond lengths of Mg-stabilised triclinic C_3S after refinement	218
Table B2.5:	O-Si-O bond angles of triclinic C_3S T_1 after refinement.....	219

LIST OF ABBREVIATIONS

AINSE	Australian Institute of Nuclear Science and Engineering
AIP	Australian Institute of Physics
ANBF	Australian National Beamline Facility (KEK)
ANSTO	Australian Nuclear Science and Technology Organisation
AM	Alumina Modulus
AMRF	Access to Major Research Facilities
ASRP	Australian Synchrotron Research Program
AXAA	Australian X-ray Analytical Association
BCE	Before Christian Era
BNL	Brookhaven National Laboratories
C ₂ S	Dicalcium silicate
C ₃ A	Tricalcium aluminate
C ₃ S	Tricalcium silicate
C ₄ AF	Tetracalcium aluminoferrite (brownmillerite)
CTL	Construction Technology Laboratories
C-S-H	Calcium silicate hydrate
DTA	Differential Thermal Analysis
ECM	European Crystallography Meeting
FOM	Figures of Merit
FWHM	Full Width at Half Maximum
GSAS	General Structure Analysis System
GUI	Graphical User Interface
HIFAR	High Flux Australian Reactor
HRPD	High Resolution Powder Diffractometer (HIFAR)
HRTEM	High Resolution Transmission Electron Microscopy
ICCC	International Congress on the Chemistry of Cement
ICNS	International Conference on Neutron Scattering
IUCr	International Union of Crystallography
IMS	Incommensurately Modulated Structures
KEK	High-Energy Accelerator Research Organisation
LSF	Lime Saturation Factor
MPC	Microscope Point Counting

NCNR	National Centre for Neutron Research
NIST	National Institute of Standards and Technology
NSLS	National Synchrotron Light Source
OPC	Ordinary Portland Cement
PCA	Portland Cement Association
PSD	Position Sensitive Detector
QPA	Quantitative Phase Analysis
SAD	Selected Area Diffraction
SCANZ	Society of Crystallography in Australia and New Zealand
SEM	Scanning Electron Microscopy
SOF	Site Occupancy Factor
SR	Silica Modulus
SSC	School on Symmetry of Crystals
SXPD	Synchrotron X-ray Powder Diffraction
TEM	Transmission Electron Microscopy
USA	United States of America
UTS	University of Technology, Sydney
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
XRPD	X-ray Powder Diffraction

ABSTRACT

Cement is the world's most popular building material, yet surprisingly its composition is not fully understood. Due to the complex nature of cement constituents, there is currently no reliable method to quantitatively determine the composition of cement. Partly this arises from the fact that the crystal structure of the main component of cement, tricalcium silicate, has not been fully determined.

There has been an increase in the use of Rietveld refinement of powder diffraction data for the analysis of cement in recent years. The method has emerged as a valuable tool for the quantitative determination of the composition of cement. A further advantage of the method is its ability to refine complex crystal structures, such as tricalcium silicate. Despite the increased application of this method, few publications exist concerning the evaluation or improvement of the method for the purpose of cement analysis.

In this work, the Rietveld method has been critically investigated as a tool for the identification and quantification of the different phases in cement clinker. Laboratory X-ray, synchrotron, neutron, and combined diffraction data are all used in the investigations. For the first time, comparisons of analysis results using various sources are made, rather than comparing the results from various methods. Inconsistencies in the results were found, and their causes were investigated and identified. The reliability of this method was shown to be dependent on the quality of the diffraction data, both in terms of the counting statistics and the resolution, and on the ability of the structures used in the Rietveld model to describe the phases in the sample.

The only previously existing structural model for triclinic tricalcium silicate is shown, in this work, inadequate as a description of the form found in cement. Consequently, the triclinic crystal structures of tricalcium silicate were re-investigated. Using synchrotron powder diffraction data, the lattice dynamics during the T_1 – T_2 transition were observed in detail for the first time. Superstructure reflections were observed for the two structures. The first model for the average sub-structure of the T_2 form is presented. Structural modulation in the T_1 form was re-investigated. The parent sub-structure, suitable for Rietveld refinement, corresponding modulation wave-vector, and superspace group of the superstructure, were identified.